



A review of biodiesel production from *Jatropha curcas* L. oil

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ABSTRACT

The demand for petroleum has risen rapidly due to increasing industrialization and modernization of the world. This economic development has led to a huge demand for energy, where the major part of that energy is derived from fossil sources such as petroleum, coal and natural gas. However, the limited reserve of fossil fuel has drawn the attention of many researchers to look for alternative fuels which can be produced from renewable feedstock.

Biodiesel has become more attractive because of its environmental benefits and it is obtained from renewable resources. There are four primary methods to make biodiesel: blending, microemulsion, pyrolysis and transesterification. The most commonly used method is the transesterification of triglycerides (vegetable oil and animal fats) with alcohol in the presence of a catalyst. There is a growing interest in using *Jatropha curcas* L. oil as the feedstock for biodiesel production because it is non-edible and thus does not compromise the edible oils, which are mainly used for food consumption. Non-edible oils are not suitable for human consumption because of the presence of toxic components. Further, *J. curcas* L. seed has a high content of oil and the biodiesel produced has similar properties to that of petroleum-based diesel.

In this paper, an attempt has been made to review the different approaches and techniques used to generate biodiesel from *Jatropha curcas* oil. The main factors affecting the biodiesel yield, for example the molar ratio of alcohol to oil, catalyst concentration, reaction temperature and reaction time are discussed. Lastly, the environmental considerations and economic aspects of biodiesel are also addressed.

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1. Introduction

The major part of all energy consumed in most parts of the world comes from fossil sources such as petroleum, coal and natural gas. However, these non-renewable sources will be exhausted in near future. Thus, the search for alternative sources of renewable and sustainable energy has gained importance with the potential to solve many current social issues such as the rising price of petroleum crude and environmental concerns like air pollution and global warming caused by combustion of fossil fuels [1].

Biodiesel fuel is of recent growing interest recently and has been strongly recommended as a substitute for petroleum diesel. The name biodiesel was introduced in the United States in the year 1992 by the National Soy Diesel Development Board which has pioneered the commercialization of biodiesel in the United State. Biodiesel can be blended with petroleum diesel as it has similar characteristics with lower hazardous exhaust emissions [21]. Biodiesel is processed from renewable biological sources such as vegetable oils and animal fats. The oils from vegetable crops and animal fats are extracted or processed to obtain the crude oil. It usually contains free fatty acids, phospholipids, sterols, water, odorants and other impurities. The free fatty acids and water contents have significant negative effects during the transesterification reaction of glycerides with alcohols using alkali or acid catalysts since they causes soap formation, consume catalysts and reduce its effectiveness and result in a lower conversion [1,2]. Many researches have been undertaken on vegetable oils as a source for diesel fuel which includes palm oil, soybean oil, sunflower oil, coconut oil, rapeseed oil and so on. However, animal fats with high saturated fatty acids which normally exist in a solid form at room temperature may cause problems in the production process, causing its processing cost to be significantly higher than for vegetable oils [5]. Thus, vegetable oils are more favourable and draw a higher attention than animal fats for the fact that they are renewable and potentially an inexhaustible source of energy [1].

This paper reviews the production of biodiesel using vegetable oils, mainly of non-edible *Jatropha curcas* as potential feedstock, the technologies implemented, the process variables, economic aspects and environmental consideration of biodiesel production.

1.1. Vegetable oils as a diesel substitute

Vegetable oils, also known as triglycerides, are becoming one of the promising renewable feedstocks for biodiesel production and have become more attractive recently because of its environmen-

tal benefits. Due to it being renewable with energy content similar to diesel fuel after undergoing some chemical modifications, vegetable oils are becoming a promising alternative as a substitute for diesel fuel. The advantages of vegetable oils are renewability, biodegradability, liquid nature-portability, higher heat content (about 88% of diesel fuel) and lower sulphur and aromatic content. Edible vegetable oils like canola, soybean, rapeseed, sunflower and corn have been used for biodiesel production and found to be good as a diesel substitute. The non-edible vegetables oils such as *madhuca indica*, *Jatropha curcas* and *Pongamia pinnata* have also found to be suitable. Edible oils are widely used and more commonly used for biodiesel production [3,4,11]. Table 1 shows the fatty acid composition for different vegetable oils. More than 95% of biodiesel production feedstock comes from edible oils in developed countries because the properties of biodiesel produced from these oils are very similar to petroleum-based diesel [5]. In view of their several advantages, vegetable oils have a great potential to replace petroleum-based fuels in the long run [1,6].

1.2. Modification of vegetable oils

It is well-known that vegetable oils are candidates as alternative fuels for diesel engines as they have high heat content. However, the direct use of these vegetable oils leads to various problems. The high viscosities of vegetable oils which are about 10 times higher than of Grade No. 2D diesel fuel leads to poor atomization of the fuel, incomplete combustion, coking of the fuel injectors and so on. These disadvantages together with the usage of unsaturated vegetable oils that may result in engine damage can be solved by chemically modifying the biodiesel, which has similar characteristics to diesel [8,9].

1.3. Pretreatment of free fatty acids

The free fatty acids (FFAs) and moisture content have negative impacts on the transesterification of glycerides with alcohol when an alkali catalyst is used. High FFA content is unfavourable in an alkali-catalysed transesterification reaction because the FFA will react with the catalyst to form soap and the separation of products will be extremely difficult, resulting in a lower yield of biodiesel. The *Jatropha curcas* oil quality will deteriorate due to improper handling and storage. Improper handling and exposure of the oil to atmospheric air and sunlight contributes to a rise in FFA concentration [20].

Table 1

Fatty acid composition for different vegetable oils [7].

Fatty acid	<i>Jatropha</i> oil	<i>Pongamia</i> (Karanja oil)	Sunflower oil	Soybean oil	Palm oil
Lauric (C ₁₂ /0)	–	–	0.5	–	–
Myristic (C ₁₄ /0)	–	–	0.2	0.1	–
Palmitic (C ₁₆ /0)	14.2	9.8	4.8	11.0	40.3
Palmitoleic (C ₁₆ /1)	1.4	–	0.8	0.1	–
Stearic (C ₁₈ /0)	6.9	6.2	5.7	4.0	3.1
Oleic (C ₁₈ /1)	43.1	72.2	20.6	23.4	43.4
Linoleic (C ₁₈ /2)	34.4	11.8	66.2	53.2	13.2
Linolenic (C ₁₈ /3)	–	–	0.8	7.8	–
Arachidic (C ₂₀ /0)	–	–	0.4	0.3	–
Behenic (C ₂₂ /0)	–	–	–	0.1	–
Saturates (%)	21.1	16.0	11.6	15.5	43.4
Unsaturates (%)	78.9	84.0	88.4	84.5	56.6

Crude *Jatropha* oil contains about 14% of FFA, which is far beyond the 1% limit for promoting transesterification reactions to occur using an alkaline catalyst [15]. It has been reported that transesterification will not occur if the FFA content in the oil is above 3% [6]. Many pretreatment methods have been proposed and established, including steam distillation, extraction by alcohol and esterification by acid catalysts. However, the esterification of FFA with methanol in the presence of acidic catalysts is the most commonly applied method because the process is simple and acid catalysts will utilize the free fatty acids in the oil and convert into biodiesel [5].

Much research work has been reported for the successful pretreatment of the high FFA of *Jatropha* oil. Patil and Deng [6] have achieved a high yield of biodiesel from *Jatropha curcas* oil with pretreatment conditions using a methanol to oil ratio of 6:1, 0.5% (v/v) of H_2SO_4 at 40 °C after 120 min. The FFA content of crude *Jatropha* oil was also reduced successfully to less than 1% with a 60%w/w methanol to oil ratio in the presence of 1%w/w of H_2SO_4 (based on weight of oil) as an acid catalyst in a 1 h reaction at 50 °C [20]. Azhari et al. [10] have conducted an optimization study to lower the FFA content of crude *Jatropha* oil via an esterification process using H_2SO_4 as a catalyst. The final FFA of the *Jatropha* oil was reduced from 25.3% to 0.5% at 60 °C under atmospheric pressure, using a 60%w/w of methanol to oil ratio, a catalyst loading of 1%w/w (based on weight of oil) and 180 min of reaction time. Further, Tiwari et al. [15] utilized the central composite rotatable design (CCRD) arrangement of response surface methodology (RSM) to predict the optimized reaction variables for the pretreatment process. The optimum combination for reducing the FFA of *Jatropha curcas* oil from 14% to less than 1% was found to be 1.43% v/v of H_2SO_4 acid catalyst, a 28% v/v methanol to oil ratio and 88 min of reaction time at 60 °C.

Another pretreatment approach for high FFA feedstock is to use a solid acid catalyst. Solid acid catalysts offer some advantages for eliminating separation, corrosion toxicity and environmental problems, but the rate of reaction in the esterification process is slower as compared to conventional liquid acid catalysts [5]. Lu et al. [14] have performed the FFA pretreatment process of crude *Jatropha curcas* oil, catalysed by liquid H_2SO_4 and a solid acid catalyst $\text{SO}_4^{2-}/\text{TiO}_2$ prepared by calcining metatitanic acid. Under the conditions of 12%w/w of methanol to oil ratio, a 1%w/w of H_2SO_4 (based on weight of oil) at 70 °C, the acid value of the oil was lowered from 14 mg KOH/g of oil to below 1 mg KOH/g of oil in 2 h. The FFA conversion achieved 95.6%. As for the solid catalyst, the optimum condition for pretreatment of *Jatropha curcas* oil were 20:1 for a molar ratio of methanol to FFA, 4 wt% of solid catalyst at 90 °C in 2 h. The conversion of FFA reached 97%. Both catalysts are able to reduce the FFA content of *Jatropha curcas* oil effectively. However, due to the lower activity of the solid catalyst, a higher molar ratio, catalyst loading and reaction temperature are required for the solid catalyst to achieve comparable efficiency.

1.4. *Jatropha curcas* as potential feedstock

Currently, the most common feedstock for biodiesel production is edible oils such as soybean, rapeseed, canola, sunflower, palm, coconut and also corn oil. However, this practice has raised objections from various organizations, claiming that biodiesel is competing for resources with the food industry. In many countries, such as India or China, edible oils are not in surplus supply and therefore it is impossible to use them for biodiesel production as they are needed more for food supply [11,12]. India accounts for 9.3% of world's total oil seed production and is considered to be one of the promising edible oil producing countries. Even so, about 46% of edible oil is imported to cater the consumption need. The same goes for China with an annual import of 400 million tons of edible oils for the country's needs [13,14].

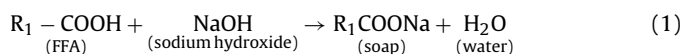
Table 2

Oil content and production of non-edible oil seeds [21].

Species	Oil fraction (%)	Seed yield ($\times 10^6$ tones/year)	Oil yield (tones/ha/year)
<i>Jatropha</i>	50–60	0.20	2.0–3.0
Mahua	35–40	0.20	1.0–4.0
Pongamia (<i>Karanja</i>)	30–40	0.06	2.0–4.0
Castor	45–50	0.25	0.5–1.0
Linseed	35–45	0.15	0.5–1.0
Others	10–50	0.50	0.5–2.0

Among various oil bearing seeds, *Jatropha curcas* has been found more suitable for biodiesel production as it has been developed scientifically to give better yield and productivity [13]. This non-edible oil is explored as a source for biodiesel production without compromising the food industry [3,4]. In addition, the oil percentage and the yield per hectare are important parameters in selecting the potential renewable source of fuel. Production of non-edible oil seeds and the percentage of oil content are given in Table 2. Non-edible oils are not suitable for human consumption because of the presence of some toxic components in the oils. Therefore, *Jatropha* oil is considered a non-edible oil due to the presence of these toxic phorbol esters [5,12].

Jatropha curcas is a drought-resistant tree belongs to the Euphorbiaceae family, which is cultivated in Central and South America, South-east Asia, India and Africa. It is easy to establish, grows almost everywhere even on gravelly, sandy and saline soils. It produces seeds for 50 years with a high oil content of about 37% or more. The oil from the seeds has valuable properties such as a low acidity, good stability as compared to soybean oil, low viscosity as compared to castor oil and better cold properties as compared to palm oil. Besides, *Jatropha* oil has higher a cetane number compared to diesel which makes it a good alternative fuel with no modifications required in the engine [3,4,13]. However, most non-edible oils contain a high level of free fatty acids (FFA) which is undesirable as it lowers the yield of biodiesel. This is because a high FFA (>1%w/w) will promote more soap formation and the separation of products will be difficult during alkali-catalysed transesterification. Eq. (1) shows the undesired saponification reaction which form soap and water when sodium hydroxide is used as the catalyst [5,20]. *Jatropha* oil contains about 14% of FFA which is far beyond the acceptable limit of a 1% FFA level. Thus, pretreatment step to reduce the FFAs of feedstock is required for a better biodiesel yield [15].



Martin et al. [16] have identified *Jatropha curcas* as the most promising oil seed for biodiesel production in Cuba after comparison with various non-edible oil seeds because of the high oil yield of *Jatropha* at about 50%. Since *Jatropha* oils consist of mainly oleic and linoleic acids which are unsaturated fatty acids, the biodiesel produced has desirable good low temperature properties. Although *Jatropha* oil also has high free fatty acid content, methods to overcome this high FFA are well developed. Thus, *Jatropha curcas* oil has been highlighted as a potential biodiesel feedstock among the non-edible oils. Table 3 tabulates the composition and characteristics of *Jatropha curcas* oil.

1.5. Other uses of *Jatropha* oil

Apart from being potential feedstock in the production of biodiesel as a diesel substitute, *Jatropha* oil has other uses such as producing soap and biocides (insecticide, molluscicide, fungicide and nematicide) [17]. Further, as the stability of biodiesel is highly critical to meet storage requirements, usually biodiesel requires the

Table 3
Composition and characteristics of *Jatropha curcas* oil [19].

Characteristic	Range
Specific gravity (g cm^{-3})	0.860–0.933
Calorific value (MJ kg^{-1})	37.83–42.05
Pour point ($^{\circ}\text{C}$)	–3
Cloud point ($^{\circ}\text{C}$)	2
Flash point ($^{\circ}\text{C}$)	210–240
Cetane value	38.0–51.0
Saponification number (mg g^{-1})	102.9–209.0
Viscosity at 30°C (cSt)	37.0–54.8
Free fatty acids % ($\text{kg kg}^{-1} \times 100$)	0.18–3.40
Iodine number (mgI g^{-1})	92.0–112.0
Acid number (mgKOH g^{-1})	0.92–6.16

addition of an antioxidant. Appropriate blends of *Jatropha* and palm biodiesel have been established in order to minimize the dosage of antioxidant needed as *Jatropha* biodiesel has good low temperature properties but a poor oxidation stability, whereas palm biodiesel has a good oxidative stability with poor low temperature properties. The blending and combinations of *Jatropha* and palm give an additive effect on these critical properties of biodiesel [18]. Moreover, direct use of *Jatropha* oil without any modifications can be used in older engines and motors equipped with current technologies such as pumps and generators running at a constant speed [19].

2. Biodiesel and its properties

Biodiesel stands for a variety of ester based oxygenated fuels derived from renewable biological sources. In other words, biodiesel refers to a vegetable oil or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, ethyl or propyl) esters or alkyl esters of fatty acids. It is a non-toxic, biodegradable and renewable fuel which can be used in compression ignition engines with little or no chemical modifications with significantly lower emissions than petroleum-based diesel when it is burned. In addition it does not contribute to the increase in carbon dioxide levels in the atmosphere and thus minimizes the intensity of the greenhouse effect. In addition, biodiesel is better than diesel fuel in terms of its properties such as sulphur content, flash point, aromatic content and biodegradability [1,6]. Table 4 represents the fuel properties of methyl esters (biodiesel) from various plant based oils. Although at present biodiesel cannot entirely replace petroleum-based diesel fuel, this alternative fuel is becoming increasingly important due to diminishing petroleum reserves that leads to a rise in petroleum prices and the environmental consequences of exhaust gases from the petroleum-fuelled engines [5,20].

2.1. Methods of biodiesel production

A number of methods are currently available that have been well established for the production of biodiesel fuel. Crude oils are worthwhile to be modified in order to reduce their viscosities so that the product obtained has suitable properties to be used as engine fuels. There are many procedures available for this

modification to produce a better quality of biodiesel. This can be accomplished in four primary ways; blending of crude oils, micro-emulsions, thermal cracking and transesterification [5,13].

2.1.1. Blending of crude oils or dilution

Crude vegetable oils can be mixed directly or diluted with diesel fuel to improve the viscosity so as to solve the problems associated with the use of pure vegetable oils with high viscosities in compression ignition engines. Caterpillar Brazil, in 1980, used a 10% mixture of vegetable oil to maintain total power without any alteration or adjustment to engines. A blend of 20% vegetable oil and 80% diesel fuel was also successfully reported [21]. Dilution with 25 parts of sunflower oils with 75 parts of diesel with a viscosity of 4.88 cSt at 40°C has been studied by Ziejewski et al. [22]. Further, it was also reported that the viscosity of 25/75 high oleic sunflower oil/diesel fuel blend was 4.92 cSt at 40°C and has passed the 200 h EMA (Engine Manufacturers' Association) test.

2.1.2. Micro-emulsification

Another approach to reduce the viscosity of vegetable oils is by microemulsion. Microemulsions are clear, stable isotropic fluids with three components: an oil phase, an aqueous phase and a surfactant. The aqueous phase may contain salts or other ingredients, and the oil may consist of a complex mixture of different hydrocarbons and olefins. This ternary phase can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles. All micro-emulsions with butanol, hexanol and octanol can meet the maximum viscosity limitation for diesel engines [13]. A microemulsion prepared by blending soybean oil, methanol, 2-octanol and cetane improver in the ratio of 52.7:13.3:33.3:1.0 has passed the 200 h EMA test [23].

2.1.3. Pyrolysis

Pyrolysis is the process of conversion of one substance into another by means of heat or with the aid of catalyst in the absence of air or oxygen. The material used for pyrolysis can be vegetable oils, animal fats, natural fatty acids and methyl ester of fatty acids [13]. Soybean oil has been thermally decomposed in air using the standard ASTM method for distillation. The viscosity of the pyrolysed soybean oil distillate is 10.2 cSt at 37.8°C , which is higher than the ASTM specified range for No. 2 diesel fuel but acceptable as still well below the viscosity of soybean oil [8].

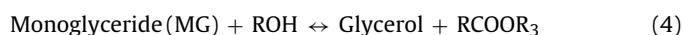
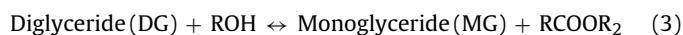
2.1.4. Transesterification

Transesterification (alcoholysis) is the chemical reaction that involves triglycerides and alcohol in the presence of a catalyst to form esters and glycerol. This transesterification involving three consecutive reversible reactions, they are the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides. Glycerides are then converted into glycerol, giving one ester in each step. A catalyst is usually used to improve and enhance the reaction rate so that the reaction can be completed in a shorter reaction time. Several catalysts have been investigated for the purpose of transesterification by many researchers. Examples are magnesium, calcium oxides and carbonates of basic and acidic

Table 4
Fuel properties of methyl ester from different oils [6].

Properties	<i>Jatropha</i> methyl ester	Karanja methyl ester	Canola methyl ester	Corn methyl ester	Biodiesel standard ASTM D 6751-02
Specific gravity	0.86–0.88	0.88–0.89	0.88–0.90	0.88–0.89	0.87–0.90
Viscosity (mm^2/s)	2.35–2.47	5.52–5.79	2.56–2.84	2.45–2.56	1.9–6.0
Calorific value (MJ/kg)	39.65–41.63	37.8–39.69	44.65–44.93	44.92–45.06	–
Acid value (mg/KOH/g)	0.61–0.66	0.72–0.76	–	–	0.8 max
Cetane number	60.74–63.27	59.68–60.90	55.90–56.10	58.37–59.00	47 min
Pour point ($^{\circ}\text{C}$)	–6 to 2	–3 to –1	–4 to –1	–5 to –2	–15 to 10

macro-reticular organic resins, alkane alumina, phase transfer catalysts, sulphuric acids, *p*-toluene sulphonic acid and dehydrating agents as a co-catalyst [24]. However, basic catalysts are usually favoured over acid catalysts because of the higher reactivity and the milder process conditions such as the lower temperature required [25]. Due to this transesterification being reversible, excess alcohol is used to shift the equilibrium towards the product. A successful transesterification reaction produces ester and crude glycerol. Though esters are the desired products of transesterification reactions, glycerin recovery is also important due to its numerous applications in daily products [26]. The transesterification reaction can be catalysed by alkalis, acids or enzymes [1]. The overall transesterification reaction is given by three consecutive and reversible equations as shown below.

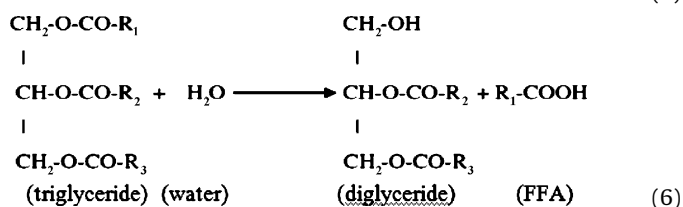
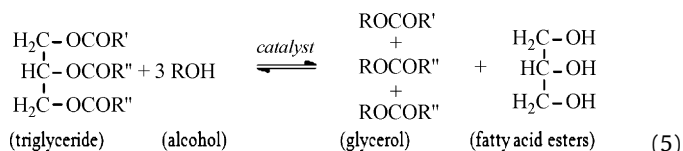


Alcohols are any organic compounds which have a hydroxyl functional group bonded to other carbons or hydrogen atoms having. Examples are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are used most frequently. However, methanol is the most preferable because of its low cost and its physical and chemical advantages as polar and short chain alcohol [1]. Methanol can also react with triglycerides quickly and easily dissolve the alkali catalyst. However, there is explosion risk associated with methanol vapors due to its low boiling point and therefore it should be handled carefully during biodiesel production [5].

2.1.4.1. Reaction mechanism of transesterification. The esters of saturated and unsaturated monocarboxylic acids with the trihydric alcohol glyceride are named triglycerides. It is the main constituent of vegetable oils and animal fats. In a transesterification reaction, the triglyceride is converted stepwise to diglyceride, monoglyceride, and lastly to glycerol in the presence of a catalyst and alcohol.

Usually, the alcohol preferred for producing biodiesel is methanol because of its low cost [5].

To complete a transesterification stoichiometrically, 1 mol of triglyceride reacts with 3 mol of alcohol to obtain 1 mol of fatty acid ester and 1 mol of glycerol, shown in Eq. (5). In practice, this molar ratio of alcohol to triglyceride is often higher to drive the equilibrium to a maximum ester yield. The reaction can be catalysed by alkalis, acids and enzymes [2]. The presence of free fatty acids and water always produces negative effects during the transesterification of vegetable oils and fats for biodiesel production, since an alkali catalyst will react with the FFA to form soap and reduce the catalyst effectiveness, which results in lower conversion. Water which originated from the oils and fats during the saponification reaction will retard the transesterification reaction through a hydrolysis reaction because it can hydrolyse triglycerides to diglycerides and form more FFA [1,5]. The hydrolysis reaction is shown in Eq. (6).



2.1.4.2. Alkali catalysed transesterification. The alkali-catalysed transesterification of vegetable oils proceeds faster than the acid-catalysed reaction and the mechanism of this alkali-catalysed transesterification has been shown in Fig. 1. The reaction mechanism is formulated in three steps. The first step is the reaction

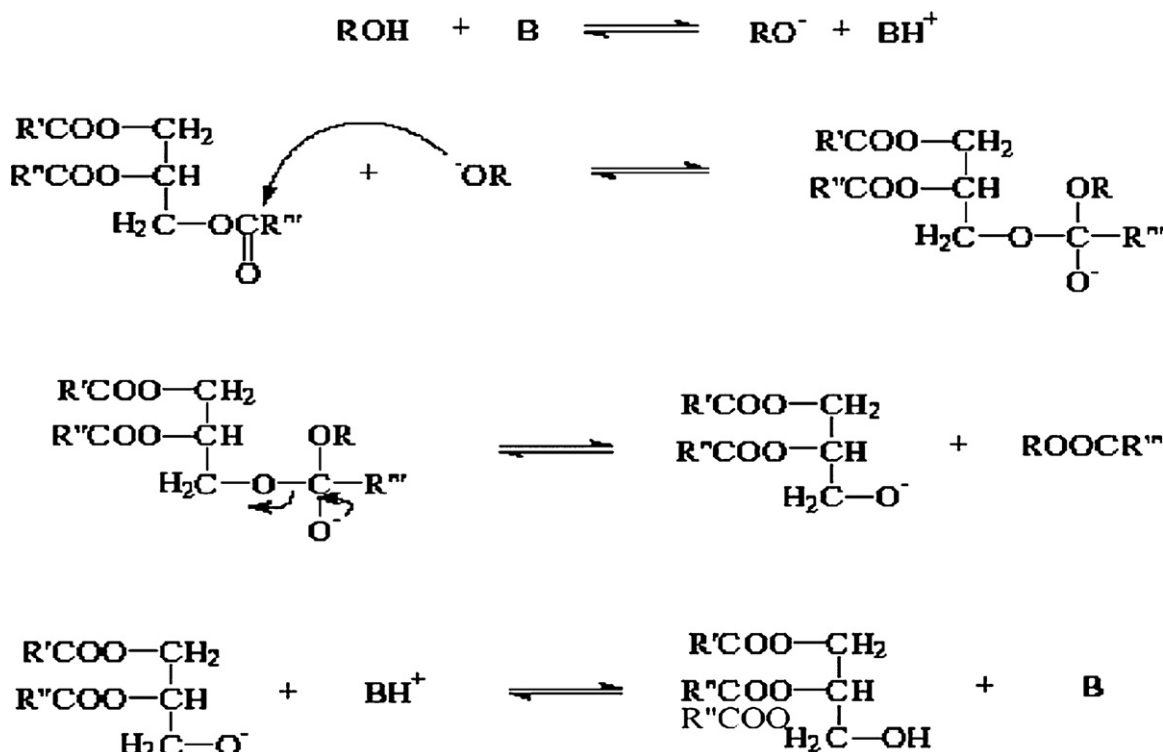


Fig. 1. Mechanism of alkali-catalysed transesterification [1] (B: base).

of the carbonyl carbon atom with the anion of the alcohol, forming a tetrahedral intermediate, from which the alkyl ester and corresponding anion of the diglycerides are formed. Another catalytic cycle is started when the catalyst reacts with a second molecule of alcohol. From there, diglycerides and monoglycerides are converted into alkyl esters and glycerol [1]. Tapanes et al. [3] have studied the reaction mechanism of the catalyst-based transesterification of *Jatropha curcas* oil and have proven the three step reaction mechanism. They reported that the reaction rate for *Jatropha* transesterification with ethanol is slightly lower than that with methanol as the stronger inductive effect of the ethyl group causes the breaking of the ethanol molecule to form an ethoxide anion which becomes more difficult than for the methoxide anion.

Many researchers have been using homogeneous alkali catalysts such as sodium hydroxide and potassium hydroxide to develop processes for the production of biodiesel from vegetable oils. Due to the low cost, both of these catalysts are most commonly used commercially [5]. However, the most active catalyst is the alkaline metal alkoxides (CH_3ONa) with very high yield of (>98%) only at low molar concentration (0.5 mol%) even with a short reaction time (30 min). Besides, potassium carbonate also gives high yields of fatty acid alkyl ester in concentration of 2 or 3 mol% with less soap formation. This is because of the formation of bicarbonate instead of water, thus the esters formed will be hydrolysed [1]. The main concern in adopting alkali catalysts in biodiesel production is the FFA content of feedstocks. A high FFA content of more than 1%w/w will enhance soap formation and the separation of end products will be hard, causing a low yield of biodiesel [20]. Therefore, the pretreatment of high FFA feedstock is required for effective alkali-catalysed transesterification to occur.

A transesterification reaction starts when the oil, alcohol and the catalyst are mixed and stirred in a reaction vessel either in a lab scale small flask or larger scale and a high yield of biodiesel can be obtained as long as the ratio of oil, alcohol and the catalyst are in the optimum ratio. Many researchers have investigated and studied the operating parameters that affecting transesterification reactions. The optimum variables for effective transesterification of *Jatropha curcas* oil are 20% methanol (by weight of oil), a molar ratio of methanol to oil of 5:1, and 1.0% of NaOH as a catalyst (by weight of oil). A maximum methyl ester yield of 98% was obtained after 90 min with a 60 °C reaction temperature and this biodiesel was found to be within the specified limits. It was also found that when the concentration of methanol and NaOH were above or below their optimum, there was no significant increase in the yield of biodiesel [27]. Due to the high FFA of *Jatropha curcas* oil, as high as 15% has been reported, a two-stage transesterification process was selected to improve the methyl ester yield. After acid pretreatment or acid catalyst esterification to reduce the FFA content in *Jatropha curcas* oil, subsequent transesterification give an optimum methyl ester yield of 90% in 2 h. The optimum methanol to oil ratio was 24%w/w and 1.4%w/w NaOH to oil as the alkaline catalyst at a reaction temperature of 65 °C [20].

The optimum transesterification conditions were also quite similar to those obtained by Lu et al. [14] in their previous work, except that by using a different type of alkali catalyst. Crude *Jatropha* oil contains many gums such as phospholipids which can deactivate the alkali catalyst, reducing the yield of methyl ester and giving a bad quality of biodiesel. The phospholipid content was significantly reduced after pretreatment operation. The yield of biodiesel from *Jatropha curcas* oil was higher than 98% which was obtained in 20 min of reaction time, using 1.3% of KOH (by weight of oil) as a catalyst and a molar ratio of methanol to oil of 6:1 at 64 °C. They also determined that the kinetics of the transesterification reaction of *Jatropha curcas* L. oil and methanol follow a pseudo-second-order mechanism.

There have been several studies on the kinetics of vegetable oils during alcoholysis reactions and the best kinetics mechanism of the transesterification of vegetable oils appeared to be second order. However, the accuracy of the final compositions reported in previous work was doubted as most of the reaction models did not consider the possible side reactions such as the effect of saponification and also the presence of FFA on the reactivity of catalysts. This shortcoming was solved when Berchmans et al. [28] investigated the kinetics of the methanolysis of a mixture of *Jatropha curcas* waste food oil via experiment and simulation. This hydroxide-catalysed methanolysis was reported to satisfy the second order kinetic reaction model with a molar ratio of methanol to oil of 6:1 and a KOH to oil mass ratio of 1 wt% under a reaction temperature of 50 °C. With 2 h of reaction time, this methanolysis of *Jatropha curcas* waste food oil was able to produce biodiesel with 97.1% purity. A better estimation was gained in this proposed kinetic model as it was able to estimate the effect of saponification and the negative effect of FFA content on the hydroxide-catalysed methanolysis.

Patil and Deng [6] also studied biodiesel production from both edible and non edible oils. These reactions were conducted by using a higher molar ratio to drive the transesterification reaction to completion at a faster rate. After undergoing acid pretreatment to reduce the high FFA in non edible *Jatropha curcas* oil, the methanol to oil molar ratio of 9:1 favoured the 2% of KOH (by weight of oil) at 60 °C. About 95% of *Jatropha* biodiesel was obtained after 120 min. Syam et al. [29] have also developed a two step process for generating biodiesel from *Jatropha curcas* oil which contains a very high level of free fatty acids. After a pretreatment process called esterification to reduce the FFA content to less than 1%, a transesterification reaction using KOH was conducted. The maximum yield of *Jatropha* methyl ester at 99% was achieved at a temperature of 65 °C, a molar ratio of methanol to oil at 6:1, a catalyst loading of 1% (by weight of oil) and a reaction time of 60 min.

Sahoo and Das [30] have also developed a method of preparation of biodiesel from non-edible oils such as *Jatropha*, *Karanja* and *Polanga*. They found that the conversion efficiency is strongly affected by the amount of alcohol because an excess of alcohol is required to shift the reaction close to completion. By concentrating on *Jatropha curcas*, the volumetric ratio of oil to methanol is 11:1, together with 1.1% of KOH by volume basis which completed the alkaline catalysed transesterification process within 120 min at 66 °C and was able to give a 93% yield of *Jatropha* methyl ester. This transesterification process improved the fuel properties of the oil with respect to density, calorific value, viscosity, flash point, cloud point and pour point. No hardware modifications of engines are required for the application of this biodiesel which has achieved relatively close fuel property values to that of diesel.

Tiwari et al. [15] have reported biodiesel production from high free fatty acid (about 14%) of *Jatropha curcas* oil. After pretreatment to reduce the FFA to less than 1% using H_2SO_4 as a catalyst, the transesterification reaction took place with a molar ratio of methanol to oil of 5:1, and using 0.55% by weight of KOH as an alkaline catalyst. Above 99% of *Jatropha* biodiesel which had properties satisfying the biodiesel standards was obtained after 24 min at a 60 °C reaction temperature. This optimization study was carried out using a central composite rotatable design (CCRD). Complete conversion of *Jatropha curcas* oil to biodiesel can be achieved with a lower catalyst loading and a shorter reaction time possibly due to the assumption of the ideal reaction in quadratic polynomial models for the transesterification and the response surface methodology based on CCRD.

In addition, a solid catalyst was also used during the transesterification process for biodiesel production. Alumina loaded with potassium nitrate which was used as a solid base catalyst for the transesterification of *Jatropha* oil with methanol. With this solid

Table 5
Alkali catalysed transesterification of *Jatropha curcas* oil with optimized reaction variables.

Alcohol	Molar ratio (alcohol to oil)	Catalyst	Catalyst amount (%wt of oil)	Optimum reaction condition	Alkyl ester yield (%)	Reference
Methanol	5:1	NaOH	1.0	60 °C, 90 min	98	[27]
Methanol	4.2:1	NaOH	1.4	65 °C, 120 min	90	[20]
Methanol	9:1	KOH	2.0	60 °C, 120 min	95	[6]
Methanol	6:1	KOH	1.0	65 °C, 60 min	99	[29]
Methanol	11:1	KOH	1.1	66 °C, 120 min	93	[30]
Methanol	5:1	KOH	0.55	60 °C, 24 min	99	[15]
Methanol	12:1	Alumina loaded with potassium nitrate	6.0	70 °C, 360 min	84	[31]

base catalyst of 6% (by weight of oil), a molar ratio of methanol to *Jatropha* oil of 12:1 and a reaction time of 6 h, it was able to achieve a biodiesel conversion of 84% at 70 °C. Further, this alumina-supported base catalyst has a reusability factor of at least three times [31]. By comparison, it was observed that a catalyst in solid form required a higher molar ratio of methanol to oil so that the equilibrium of this reversible transesterification reaction will tend to shift towards the direction of ester formation. The catalyst loading and reaction time was also reported to be much higher than the conventional base-catalysed transesterification where the catalysts were in liquid form in order to achieve a comparable yield of methyl ester. Therefore a solid base catalyst is less attractive or preferable to be implemented on an industrial scale for biodiesel production due to its lower catalyst activity as well as efficiency. On the other hand, the benefit of using a solid base catalyst is the ease of separation from the reaction mixture using only simple filtration and solid base catalysts are easily generated leading to cheaper operations [25]. Table 5 summarises the optimized conditions for alkali catalysed transesterification of *Jatropha curcas* oil.

2.1.4.3. Acid catalysed transesterification. The acid-catalysed transesterification process is not very popular as a base-catalysed process due to the slower reaction rate and the high methanol to oil molar ratio requirement. In addition, an acid-catalyst has a lower activity and the transesterification reaction occurs at a higher process temperature than for the base-catalysed reaction [25]. The use of solid acid catalysts still requires a higher temperature and pressure in order to be more effective. Moreover, a long reaction time makes the process impractical and uneconomical [33]. On the other hand, the advantage of using an acid-catalysed transesterification is the tolerance towards the presence of high FFAs in the feedstock. In fact, acid catalysts can directly produce biodiesel from low-cost lipid feedstock with an FFA greater than 6% [32]. Liquid acid catalysts such as sulphuric acid have a tolerance and less sensitive to FFA and can simultaneously conduct esterification and transesterification by giving a high yield in esters [33]. Other acid catalysts included sulphonic acid, phosphoric acid, hydrochloric acid, Lewis acids (AlCl_3 or ZnCl_2), etc. [25].

The mechanism of acid-catalysed transesterification of vegetable oil is shown in Fig. 2. The protonation of the carbonyl group of the ester promotes the formation of carbocation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate will eliminate glycerol to form a new ester and to regenerate the catalyst. Acid-catalysed transesterification should be carried out in the absence of water [1].

Acid catalytic transesterification of vegetable oils has been carried out and reported by several researchers. Solid superacid catalysts of sulphated tin and zirconium oxides and tungstated zirconia were used in the transesterification of soybean oil with methanol at 475–575 K, which have been reported by Schuchardt et al. [35]. Furthermore, the conversion of canola oil into methyl ester has achieved 98% at 24:1 with a methanol to oil ratio using 5%

AlCl_3 (by weight based on oil) as a catalyst. The reaction was completed at 110 °C and 18 h with tetrahydrofuran as the co-solvent. Results showed that ZnCl_2 was less effective in catalysing the transesterification of canola oil into methyl ester owing to its lower acidity than AlCl_3 [36]. In addition, the one-step conversion of soybean oil into biodiesel catalysed by 2.0 M of trifluoroacetic acid has reached as high as 98.4% with a 20:1 of methanol to oil ratio at a temperature of 120 °C in about 5 h of reaction time [33].

When focusing on *Jatropha curcas* oil as the feedstock to synthesize *Jatropha* biodiesel, acid-catalysed transesterification is hardly performed or proposed by other researchers as an alkali-catalyst is considered as the most favourable. Shuit et al. [11] have reported on the reactive extraction using an acidic catalyst to produce biodiesel from *J. curcas* L. seeds. Concentrated sulphuric acid was used as a catalyst since the crude *Jatropha curcas* oil contains a high FFA at about 15%. About 99.8% of *Jatropha* methyl ester was obtained by using a size of the *Jatropha* seed of less than 0.355 mm and using n-hexane as a co-solvent, a reaction temperature of 60 °C, a reaction period of 24 h, a methanol to seed ratio of 7.5 ml/g (approximate ratio of 5.9:1) and 15 wt% of H_2SO_4 (by weight of *Jatropha* seed). They proved that the single step reactive extraction process can achieve a comparable yield of biodiesel and has the potential of reducing the cost of production as compared to the two step conventional method reported in the literature. Thus, this acid-catalysed reactive extraction to produce biodiesel in a single step could be a breakthrough technology and should gain the interest of more researchers to further investigate using this technology. Table 6 tabulates the optimized conditions for acid catalysed transesterification of *Jatropha curcas* oil.

2.1.4.4. Enzyme-catalysed transesterification. Enzymatic transesterification using a lipase catalyst looks attractive due to the easy product separation, minimal wastewater treatment needed, easy glycerol recovery and absence of side reactions [37]. Lipases are known to have a tendency to act on long chain fatty alcohol better than on the short chain type. In the biotechnical process, mild reaction conditions are usually conducted. However, a biocatalyst is more expensive and regeneration and reuse of it is of limited with a long operating time required [33]. The reaction yields from enzyme-catalysed transesterification are as yet still unfavourable compared to the base-catalysed reactions and thus render the process impractical and uneconomical [1,33].

Several studies of the lipase-catalysed process for biodiesel production were proposed. Immobilized lipases were used to facilitate its recovery after the reaction for repeated usage. Novozym 435 (*Candida Antarctica* immobilized on acrylic resin) was reported to be an effective lipase catalyst for biodiesel fuel production [38]. However, the complexity of the lipase purification process has restricted its use in industrial applications. To overcome this, Tamalampudi et al. [39] have recommended the production of biodiesel from *Jatropha* oil using the whole cell of lipase producing *Rhizopus oryzae* (ROL) immobilized onto biomass support particles

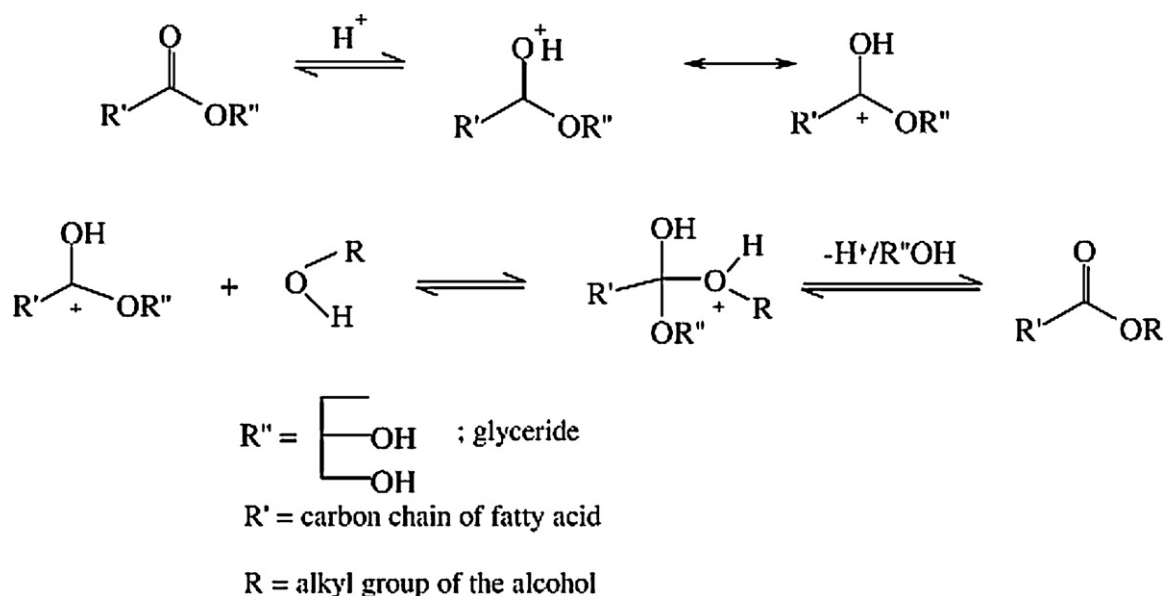


Fig. 2. Mechanism of acid-catalysed transesterification of vegetable oils [34].

Table 6

Acid catalysed transesterification of *Jatropha curcas* oil with optimized reaction variables.

Alcohol	Molar ratio (alcohol to seed)	Catalyst	Catalyst amount (%wt of seed)	Optimum reaction condition	Alkyl ester yield (%)	Reference
Methanol	5.9:1	H ₂ SO ₄	15.0	60 °C, 24 h	99.8	[11]

(BSPs). They concluded that whole cell *R. oryzae* immobilized onto BSP is able to catalyse the methanolysis of *Jatropha* oil more efficiently than Novozym 435 in the production of biodiesel. The yield of methyl ester achieved was 80% after 60 h using 4% of ROL (by weight of oil) in the presence of 5% (v/v) added water, methanol to oil ratio of 1:1 and reaction temperature of 30 °C. Furthermore, it was economical and practical as the lipase exhibited more than 90% of its initial activities after five repeated cycles of usage.

In addition, the activity of other lipase was also investigated in the preparation of biodiesel from *Jatropha* oil. 10% of *Pseudomonas cepacia* lipase (by weight of oil) immobilized on celite has the best yield of 98% of biodiesel produced in the presence of 4–5% (w/w) water in 8 h and at 50 °C. The molar ratio of ethanol to oil was 4:1. It was shown that commercial grade ethanol can be used instead of the expensive grade ethanol which is fairly important in the effort to have an economical route of biodiesel production. This biocatalyst was found to be usable for up to four times without the loss of its activity [12]. Table 7 summarises the optimized conditions for enzyme catalysed transesterification of *Jatropha curcas* oil.

2.1.4.5. Non-catalytic supercritical alcohol transesterification. The transesterification of vegetable oils with non-catalytic supercritical methanol has been developed to provide a new way of producing biodiesel. Under this supercritical condition, the transesterification process can be completed in minutes with a relatively high yield. It was observed that by increasing the reaction temperature to a supercritical temperature had a favourable influence on ester conversion [1]. Moreover, this method has made purification of

biodiesel much easier as no catalyst was required during the supercritical transesterification process thus preventing soap formation or saponification to occur. The presence of water which has a negative impact in conventional transesterification is no longer an issue during the formation of methyl esters in supercritical methanol method [1,9].

However, the drawbacks of this supercritical transesterification process are due to the high temperature and pressure that result in the high cost of the apparatus. Co-solvents, such as carbon dioxide, hexane, propane, calcium oxide and subcritical alcohol have been added into the reaction mixture to lower the operating temperature, pressure and the amount of alcohol needed [32].

Much research work has been carried out for biodiesel production from various feedstocks under different conditions using supercritical alcohol. As for *Jatropha* oil, Hawash et al. [40] have revealed that a 100% yield of *Jatropha* biodiesel can be obtained in 4 min using supercritical methanol at a temperature of 593 K (320 °C) and under a pressure of 8.4 MPa. The molar ratio of methanol to oil was 43:1. The separation of products as well as by-products can be achieved efficiently under such supercritical conditions because no catalyst is needed and hence there is no soap formation. Even though supercritical alcohol methods in biodiesel production have a simple reaction with a shorter reaction time and no catalyst is required compared to the conventional methods proposed, the safety aspect should be taken into consideration due to high reaction temperature and pressure during the operation. Similarly, Ilham and Saka [41] also reported a new potential method for biodiesel production from *Jatropha curcas* oil by utilizing supercrit-

Table 7

Enzyme catalysed transesterification of *Jatropha curcas* oil with optimized reaction variables.

Lipase	Lipase amount (%wt of oil)	Alcohol	Molar ratio (alcohol to oil)	Optimum reaction condition	Solvent	Alkyl ester yield (%)	Reference
<i>Rhizopus oryzae</i>	4.0	Methanol	1:1	30 °C, 60 h	Water	80	[39]
<i>Pseudomonas cepacia</i>	10.0	Ethanol	4:1	50 °C, 8 h	Water	98	[12]

Table 8
Supercritical transesterification of *Jatropha curcas* oil with optimized reaction variables.

Reactant	Molar ratio	Supercritical condition	Reaction time (min)	Alkyl ester yield (%)	Reference
Methanol	43:1 (methanol to oil)	320 °C, 8.4 MPa	4	100	[40]
Dimethyl carbonate	14:1 (dimethyl carbonate to oleic acid)	300 °C, 9 MPa	15	97	[41]
Methanol	3:1 (methanol to oil)	290 °C, 11 MPa	15	99	[42]

ical dimethyl carbonate at 300 °C and 9 MPa for 15 min to achieve a comparably high yield of methyl ester at 97% by weight. The molar ratio of dimethyl carbonate to oleic acid was 14:1. Before the supercritical dimethyl carbonate treatment, the *Jatropha* oil was treated for 25 min in subcritical water at 270 °C and 27 MPa with a molar ratio of water to oil of 217:1 to produce fatty acids and glycerol. The high content of free fatty acids in *Jatropha curcas* oil resulting from the hydrolysis reaction contributes to complete conversion of biodiesel with a shorter reaction time in a milder supercritical condition. However, this high content of free fatty acids in *Jatropha* oil is not suitable when alkali-based catalysts are applied. Another attempt of supercritical carbon dioxide extraction of oil from *Jatropha curcas* seed, followed by subsequent subcritical hydrolysis and supercritical methylation of the extracted *Jatropha curcas* oil has been reported to achieve biodiesel conversion of 99% at 11 MPa and 563 K (290 °C). The molar ratio of methanol to oil was 3:1 and the reaction lasted 15 min. Carbon dioxide was used as the co-solvent, which has proven effective in reducing the supercritical temperature and accelerating the reaction rate during supercritical methylation process [42]. Table 8 tabulates the optimized conditions for supercritical transesterification of *Jatropha curcas* oil.

2.1.4.6. Ultrasound assisted transesterification. Ultrasound is defined as a sound of a frequency beyond that to which a human ear can respond. The range of ultrasound is between 20 kHz to beyond 100 MHz and it has proven to be a useful tool in enhancing the reaction rates in many reacting systems. During the application in transesterification, ultrasonication provides the mechanical energy for mixing and the activation energy needed to start the transesterification reaction [43]. Furthermore, ultrasonication increases the chemical reaction speed, the efficient molar ratio of methanol to oil, the yield of transesterification of vegetable oils and animal fats into biodiesel with less energy consumption than for the conventional mechanical stirring method [44].

Transesterification of vegetable oils using ultrasonic irradiation has been implemented in order to reduce the processing time and phase separation time. Kumar et al. [45] have reported a new ultrasound-assisted transesterification method for biodiesel production from *Jatropha curcas* oil by using Na supported on SiO₂ as a catalyst. A maximum yield of more than 98.53% of *Jatropha* biodiesel was obtained with a methanol to oil ratio of 9:1, 3% of solid Na/SiO₂ (by weight of oil), a 50% of ultrasonic wave amplitude, a 0.7 Hz ultrasonic irradiation pulse and a reaction time of 15 min. It was beneficial as a fast alternative to the conventional transesterification process with a high product yield, with simple and mild reaction conditions as well as catalyst reusability. The acid value, viscosity, density and cetane number of the *Jatropha curcas* methyl ester obtained were within the American Standard Test Method (ASTM) limits. They also suggested that this method can be used effectively for continuous production of biodiesel in a continuous stirred tank reactor (CSTR) and plug flow system.

3. Main factors affecting the yield of biodiesel

There are few important variables that influence the transesterification reaction. In order to obtain maximum yield of biodiesel, these variables must be at their optimum.

3.1. Reaction temperature

The rate of reaction is strongly affected by the reaction temperature. A higher reaction temperature can decrease the viscosities of oils and result in an increase in reaction rate as more energy is being supplied for the reaction to occur. Thus the yield of the biodiesel product is improved. However, the reaction temperature must be less than the boiling point of alcohol (boiling point of methanol is at 60–70 °C at atmospheric pressure) to ensure the alcohol will not be lost through vaporization. Also, the yield of biodiesel decreases if the reaction temperature goes beyond its optimum level because a higher reaction temperature will accelerate the saponification reaction which results in a lower yield. Depending on the types of oil, the maximum yield is obtained at temperatures ranging from 60 to 80 °C [5,9].

3.2. Molar ratio of alcohol to oil

The stoichiometric ratio for the transesterification reaction involves 3 mol of alcohol and 1 mol of triglyceride to produce 3 mol of fatty acid ester and 1 mol of glycerol. Excess alcohol is used during transesterification to ensure that the oils will be completely converted to ester due to the forward reaction being more favourable. Furthermore, a higher alcohol to triglyceride ratio can result in a greater ester conversion in a shorter time. The molar ratio is associated closely with the type of catalyst used. For base-catalysed transesterification where the free fatty acids are less than 1% after pretreatment, a molar ratio of methanol to oil of 5:1 or 6:1 is sufficient to convert *Jatropha* oil to biodiesel [14,15,27]. However, where the percentage of free fatty acids in oils is high, a molar ratio as high as 20:1 or 24:1 is needed when using acid-catalysed transesterification [33,36].

3.3. Concentration of catalyst

Catalyst concentration can affect the yield of the biodiesel produced. As mentioned earlier, basic catalysts are usually preferred to acid catalysts because of the higher reactivity and the lower process temperature required [25]. Freedman et al. [46] found that sodium methoxide was more effective than sodium hydroxide because of the reduced amount of water produced upon mixing sodium hydroxide with methanol. As the catalyst concentration increases, the conversion of triglycerides and the yield of biodiesel also increased. A concentration of NaOH in the range of 1.0–1.4% (w/w) has been found to produce 90–98% conversion from *Jatropha* oil to methyl ester [20,27]. As for the concentration of KOH ranging from 0.55 to 2.0% (w/w), 95–99% of *Jatropha* biodiesel has been obtained [6,14,15,28]. However, the yield of biodiesel was reduced if the alkali catalysts were added above their optimum concentration as this causes more soap formation [5].

3.4. Reaction time

The conversion rate increases with reaction time. Initially the reaction was slow due to the mixing and dispersion of alcohol into the oil as reported by Freedman et al. After some time, the reaction proceeds faster until maximum yield is reached [46]. For base-catalysed transesterification, the yield of biodiesel reaches

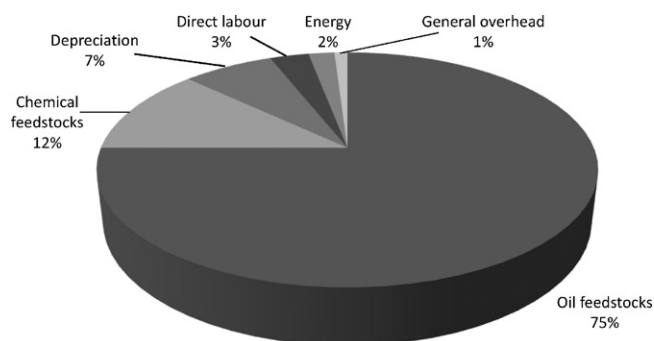


Fig. 3. General cost breakdown of biodiesel production [48].

maximum at a reaction time of 120 min or less [20,28,30]. Acid-catalysed transesterification requires an even longer reaction time than the base-catalysed reaction because base catalysts are usually exhibit a higher reactivity than acid catalysts [25]. The reaction time needed during the conversion of triglycerides to biodiesel may range from 18 to 24 h as investigated in previous work [11,36]. However, an excess reaction time will lead to a reduction in the product yield due to the backward reaction of transesterification, causing more fatty acids to form soaps [5].

4. Economic aspects of biodiesel

Biodiesel has become more attractive recently due to its environmental benefits and the fact that it is sustainable because it is made from renewable sources. It has several outstanding advantages as an effective alternative fuel with a lower level of pollution. However, the cost of biodiesel is the major challenge as it varies depending on the feedstock, processing, transporting, the price of crude petroleum and others [1,21].

Vegetable oils are renewable and a potential source of energy content close to petroleum diesel fuel. However, the relatively high cost of vegetable oils (about four times the cost of diesel in India) has made biodiesel not economically feasible as the methyl ester produced from these edible oils is much more expensive and cannot compete economically with diesel fuels. The cost of raw materials accounts for 60–75% of the total cost of biodiesel fuel [1,21]. Leduc et al. [47] also reported a rise of 40% in biodiesel cost associated with an increase in the feedstock cost. Lim and Teong [48] also determined that the price of the feedstock alone accounts for more than 75% of the overall cost of biodiesel production which is shown in Fig. 3. With the recent increase in the petroleum prices and the uncertainties of petroleum availability due to depletion, biodiesel is still gaining interest. Therefore there is a need to explore alternative feedstocks to lower the cost of biodiesel production.

The selection of the best feedstock selection is essential to ensure and keep the biodiesel production cost low. Non edible oils such as jatropha, pongamia, karanja as well as waste cooking oil and animal fats can be converted into biodiesel. Nevertheless, the problem associated with these low-cost oils is often the high content of free fatty acids (FFA). Pretreatment has to be carried out in order to remove these free fatty acids before proceeding to subsequent transesterification. In terms of production cost, there are two aspects, the transesterification process and glycerol recovery. A continuous transesterification process with a shorter reaction time and a greater production capacity can lower the production cost. In addition, the cost of biodiesel fuel can be lowered if a biodiesel plant has its own glycerol recovery facility [21]. Leduc et al. [47] have also studied the factors involved in producing biodiesel from *Jatropha curcas* at a competitive cost and to minimize the overall costs in order to fulfill the demand as a potential diesel substitute.

The results stated that the biomass cost has the most influence on the biodiesel production cost (a rise of 40% in biodiesel cost), while the investment cost, the transportation cost and the glycerol (by product) price are less important. As for different biodiesel blends, the biodiesel costs do not differ much, but the emission compositions that contribute to environmental pollution should be the major deciding factor [47].

For biodiesel to be well established and accepted in the market, many factors and issues must be overcome. The key issues are the utilization of low cost feedstock such as non-edible vegetable oils or waste oils, improving the efficiency of the production process through optimum process variables and conditions and minimizing the cost of the catalysts used though the regeneration of catalysts. Further, the emission qualities of biodiesel can be improved through a blending process in order to remain acceptable to the public. Further development of the use of the by-product such as glycerol will enhance the economic viability of the overall biodiesel production process. On top of that, strong government support and policy enforcement will play an important role in determining the success of the biodiesel industry. The biodiesel industry is still behind the conventional oil and gas industry in terms of financial profitability and infrastructure support. Thus, the implementation of a carbon tax that rewards the usage of renewable fuels usage including biodiesel and its blends over fossil diesel can stimulate the biodiesel industry. Mechanisms to encourage a wider participation of the global community towards the reduction of greenhouse gas (GHG) emissions will further promote the use of renewable fuels [48,51].

5. Environmental considerations

Biodiesel is considered to be carbon neutral because the carbon dioxide released into the atmosphere during its consumption as a fuel is been recycled and reused for the growth of vegetable oil crops [9]. Biodiesel has a higher cetane number than diesel because of its long chain fatty acids with 2–3 double bonds, it is without aromatics and contains 10–11% oxygen by weight. These characteristics of biodiesel reduce the emission of carbon dioxide (CO), hydrocarbon (HC) and particulate in the exhaust gas compared to diesel fuel [49].

Biodiesel has a lower energy content than petrodiesel, and so it will require more fuel to produce the same energy compared to petrodiesel fuel. Rajesh et al. [50] has mentioned that the burning rate of biodiesel is reduced by about 11% compared to diesel. However, in view of the environmental impact through emissions, biodiesel has been reported to emit lesser pollutants compared to diesel. The comparison of biodiesel emission and conventional diesel is given in Table 9.

The emission performance of each methyl ester varies according to the properties of the feedstock [51]. Generally, all emissions associated with 100% pure biodiesel (B100) are lower than conventional diesel except for NO_x. The NO_x emissions from pure biodiesel increase on average by 10% depending on the combustion characteristics of the engine and the testing procedure. Besides, sulphur emissions are essentially eliminated with pure biodiesel as compared to diesel. Moreover, the exhaust emissions of total

Table 9
Emission comparison of biodiesel and diesel [52].

Emission type	B100 (%)	B20 (%)
Total unburned hydrocarbons	–67	–20
Carbon monoxide	–48	–12
Particulate	–47	–12
NO _x	+10	+2 to –2
Sulphates	–100	–20
PAH (polycyclic aromatic hydrocarbons)	–80	–13
nPAH (nitrated PAH's)	–90	–50

hydrocarbons, carbon monoxide and also particulates are lower on average by 67%, 48% and 47% respectively for biodiesel compared to diesel fuel. The level of polycyclic aromatic hydrocarbons (PAH) which have been identified as potential cancer causing compounds also shows a decrease of 80% in biodiesel emission [52].

6. Conclusions

The problem of diminishing petroleum reserves and the increasing awareness of environmental pollution from petroleum fuel emissions have led to the urge to find renewable alternative fuels as a substitute for petroleum based fuel. Biodiesel, which has environmental benefits and is produced from renewable resources, has become more attractive recently. *Jatropha curcas* is becoming a potential feedstock for biodiesel production due to its suitable characteristics. *Jatropha* oil has a higher cetane number [51] as compared to diesel [46–50] and thus it is an ideal alternative fuel and requires no modification of the engine to run.

There are several methods proposed for biodiesel production, of which the transesterification of vegetable oils is the most preferable because of its renewability and sustainability. The factors that affect transesterification are the molar ratio of alcohol to glyceride, the amount of catalyst required, the reaction temperature, the reaction time and the amount of free fatty acids in the feedstock. Apart from conventional techniques for biodiesel production, the application of supercritical alcohol and ultrasound has been explored to achieve enhancement of the final product yield.

The cost of biodiesel is the major challenge and obstacle facing the commercialization of the products. This is due to the relatively high cost of vegetable oils as raw materials in biodiesel production and has made biodiesel not economically feasible. A continuous transesterification process can be one of the choices to lower the production cost. Also, the recovery of high quality by products such as glycerol for other useful applications is a possible way to offset the high cost of vegetable oils as feedstock. Further development and effort is required with more advanced techniques or methods for effective biodiesel production to have comparable characteristics to diesel, and which are sustainable and economically feasible. The emission compositions of biodiesel have contributed much in reducing environmental pollution where they are used, which has gained much attention and concern nowadays and eventually should be the majority point of view. Therefore, continuous development and improvement of biodiesel is needed in producing cleaner emissions with less impact on the environment and at a much lower cost compared to fossil fuels. Finally, government incentives can spur the industry and result in maintaining biodiesel as a sustainable fuel.

References

- [1] Demirbas A. Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Progress in Energy and Combustion Science* 2005;31:466–87.
- [2] Ma F, Hanna MA. Biodiesel production: a review. *Bioresource Technology* 1999;70:1–15.
- [3] Tapanes NCO, Gomes Aranda DA, de Mesquita Carneiro JW, Ceva Antunes OA. Transesterification of *Jatropha curcas* oil glycerides: theoretical and experimental studies of biodiesel reaction. *Fuel* 2008;87:2286–95.
- [4] Divakara BN, Upadhyaya HD, Wani SP, Laxmipathi Gowda CL. Biology and genetic improvement of *Jatropha curcas* L.: a review. *Applied Energy* 2010;87:732–42.
- [5] Leung DY, Wu X, Leung MKH. A review on biodiesel production using catalyzed transesterification. *Applied Energy* 2010;87:1083–95.
- [6] Patil PD, Deng S. Optimization of biodiesel production from edible and non-edible vegetable oils. *Fuel* 2009;88:1302–6.
- [7] Sarin R, Sharma M, Sinharay S, Malhotra RK. *Jatropha*-Palm biodiesel blends: an optimum mix for Asia. *Fuel* 2007;86:1365–71.
- [8] Schwab AW, Bagby MO, Freedman B. Preparation and properties of diesel fuels from vegetable oils. Peoria, IL, USA: Northern Regional Research Center, Agricultural Research Service, US Department of Agriculture; 1987.
- [9] Barnwal BK, Sharma MP. Prospects of biodiesel production from vegetable oils in India. *Renewable and Sustainable Energy Reviews* 2005;9:363–78.
- [10] Azhari, Faiz M, Yunus R, Ghazi TIM, Yaw TCS. Reduction of free fatty acids in crude *Jatropha curcas* oil via an esterification process. *International Journal of Engineering and Technology* 2008;5(2):92–8.
- [11] Shuit SH, Lee KT, Kamaruddin AH, Yusup S. Reactive extraction and in situ esterification of *Jatropha curcas* L. seeds for the production of biodiesel. *Fuel* 2009 [Short communication].
- [12] Shah S, Gupta MN. Lipase catalyzed preparation of biodiesel from *Jatropha* oil in a solvent free system. *Process Biochemistry* 2007;42:409–14.
- [13] Jain S, Sharma MP. Prospects of biodiesel from *Jatropha* in India: a review. *Renewable and Sustainable Energy Reviews* 2010;14:763–71.
- [14] Lu H, Liu Y, Zhou H, Yang Y, Chen M, Liang B. Production of biodiesel from *Jatropha curcas* L. oil. *Computers and Chemical Engineering* 2009;33:1091–6.
- [15] Tiwari AK, Kumar A, Rahman H. Biodiesel production from *Jatropha* oil (*Jatropha curcas*) with high free fatty acids: an optimized process. *Biomass and Bioenergy* 2007;31:569–75.
- [16] Martin C, Moure A, Martin G, Carrillo E, Dominguez H, Parajo JC. Fractional characterization of *Jatropha*, neem moringa, trisperma, castor and candlenut seeds as potential feedstocks for biodiesel production in Cuba. *Biomass and Bioenergy* 2010;34:533–8.
- [17] Shanker C, Dhyani SK. Insect pests of *Jatropha curcas* L. and potential for their management. *Current Science* 2006;91:162–3.
- [18] Sarin R, Sharma M, Sinharay S, Malhotra RK. *Jatropha*-palm biodiesel blends: an optimum mix for Asia. *Fuel* 2007;86:1365–71.
- [19] Achten WMJ, Verchot L, Franken YJ, Mathijs E, Singh VP, Aerts R, et al. *Jatropha* bio-diesel production and use. *Biomass and Bioenergy* 2008;32:1063–84.
- [20] Berchmans HJ, Hirata S. Biodiesel production from crude *Jatropha curcas* L. seed oil with a high content of free fatty acids. *Bioresource Technology* 2008;99:1716–21.
- [21] Singh SP, Singh D. Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of biodiesel: a review. *Renewable and Sustainable Energy Reviews* 2010;12:200–16.
- [22] Ziejewski M, Goettler H, Pratt GL. International congress and exposition. Detroit, MI; 24–28 February 1986 [Paper No. 860301].
- [23] Goering CE. Final report for project on effect of non petroleum fuels on durability of direct-injection diesel engines under contract 59-2171-1-6-057-0. Peoria IL: USDA, ARS; 1984.
- [24] Nye MJ, Southwell PH. Esters from rapeseed oil as diesel fuel. In: *Proceedings of vegetable oil as diesel fuel*, Seminar III. 1983.
- [25] Georgogianni KG, Katsoulidis AK, Pomonis PJ, Manos G, Kontominas MG. Transesterification of rapeseed oil for the production of biodiesel using homogeneous and heterogeneous catalysis. *Fuel Processing Technology* 2009;90:1016–22.
- [26] Ramadhas AS, Jayaraj S, Muraleedharan C. Biodiesel production from high FFA rubber seed oil. *Fuel* 2005;84:335–40.
- [27] Chitra P, Venkatachalam P, Sampathrajan A. Optimisation of experimental conditions for biodiesel production from alkali-catalysed transesterification of *Jatropha curcas* oil. *Energy for Sustainable Development* 2005;9:13–8.
- [28] Berchmans HJ, Morishita K, Takarada T. Kinetic study of hydroxide-catalyzed methanolysis of *Jatropha curcas*-waster food oil mixture for biodiesel production. *Fuel* 2010.
- [29] Syam AM, Yunus R, Ghazi TIM, Yaw TCS. Methanolysis of *Jatropha* oil in the presence of potassium hydroxide catalyst. *Journal of Applied Science* 2009;9(17):3161–5.
- [30] Sahoo PK, Das LM. Process optimization for biodiesel production from *Jatropha*, *Karanja* and *Polanga* oils. *Fuel* 2009;88:1588–94.
- [31] Vyas AP, Subrahmanyam N, Patel PA. Production of biodiesel through transesterification of *Jatropha* oil using $\text{KNO}_3/\text{Al}_2\text{O}_3$ solid catalyst. *Fuel* 2008.
- [32] Vyas AP, Verma JL, Subrahmanyam N. A review on FAMA production processes. *Fuel* 2010;89:1–9.
- [33] Miao X, Li R, Yao H. Effective acid-catalyzed transesterification for biodiesel production. *Energy Conversion and Management* 2009;50:2680–4.
- [34] Meher LC, Sagar DV, Naik SN. Technical aspects of biodiesel production by transesterification—a review. *Renewable and Sustainable Energy Reviews* 2006;10:248–68.
- [35] Schuchardt U, Ricardo Sercheli R, Vargas RM. Transesterification of vegetable oils: a review. *Journal of the Brazilian Chemical Society* 1998;9:199–210.
- [36] Soriano Jr NU, Venditti R, Argyropoulos DS. Biodiesel synthesis via homogeneous Lewis acid-catalyzed transesterification. *Fuel* 2009;88:560–5.
- [37] Raman JK, Sariah A, Denis P, Chan ES, Pogaku R. Production of biodiesel using immobilized lipase—a critical review. *Critical Reviews in Biotechnology* 2008;28:253–64.
- [38] Shimada Y, Watanabe Y, Samukawa T, Sugihara A, Noda H, Fukuda H, et al. Conversion of vegetable oil to biodiesel using immobilized *Candida Antarctica* lipase. *Journal of the American Oil Chemists Society* 1999;76:789–93.
- [39] Tamalampudi S, Talukder MR, Hama S, Numata T, Kondo A, Fukuda H. Enzymatic production of biodiesel from *Jatropha* oil: a comparative study of immobilized-whole cell and commercial lipases as a biocatalyst. *Biochemical Engineering Journal* 2008;39:185–9.
- [40] Hawash S, Kamal N, Zaher F, Kenawi O, El Diwani G. Biodiesel fuel from *Jatropha* oil via non-catalytic supercritical methanol transesterification. *Fuel* 2009;88:579–82.
- [41] Ilham Z, Saka S. Two-step supercritical dimethyl carbonate method for biodiesel production from *Jatropha curcas* oil. *Bioresource Technology* 2010;101:2735–40.

- [42] Chen CH, Chen WH, Chang CMJ, Lai SM, Tu CH. Biodiesel production from supercritical carbon dioxide extracted *Jatropha* oil using subcritical hydrolysis and supercritical methylation. *Journal of Supercritical Fluids* 2010;52: 228–34.
- [43] Singh AK, Fernando SD, Hernandez R. Base-catalyzed fast transesterification of soybean oil using ultrasonication. *Energy and Fuels* 2007;21:1161–4.
- [44] Ji JB, Wang JL, Li YC, Yu YL, Xu ZC. Preparation of biodiesel with the help of ultrasonic and hydrodynamic cavitation. *Ultrasonics* 2006;44:411–4.
- [45] Kumar D, Kumar G, Poonam, Singh CP. Ultrasonic-assisted transesterification of *Jatropha curcas* oil using solid catalyst, Na/SiO₂. *Ultrasonics Sonochemistry* 2010;0300, doi:10.1016/j.ultsonch.2010.
- [46] Freedman B, Pryde EH, Mounts TL. Variables affecting the yields of fatty esters from transesterified vegetable oils. *Journal of the American Oil Chemists Society* 1984;61:1638–43.
- [47] Leduc S, Natarajan K, Dotzauer E, McCallum I, Obersteiner M. Optimizing biodiesel in India. *Applied Energy* 2009;86:125–31.
- [48] Lim S, Teong LK. Recent trends, opportunities and challenges of biodiesel in Malaysia: an overview. *Renewable and Sustainable Energy Reviews* 2010;14:938–54.
- [49] Graboski MS, McCormick RL. Combustion of fat and vegetable-oil derived fuels in diesel engines. *Progress in Energy and Combustion Sciences* 1998;24:125–64.
- [50] Rajesh S, Raghavan V, Shet USP, Sundararajan T. Analysis of quasi-steady combustion of *Jatropha* biodiesel. *International Communications in Heat and Mass Transfer* 2008;35:1079–83.
- [51] Janaun J, Ellis N. Perspectives on biodiesel as a sustainable fuel. *Renewable and Sustainable Energy Reviews* 2010;14:1312–20.
- [52] Biodiesel Emissions. http://www.biodiesel.org/pdf_files/fuelsheets/emissions.PDF [accessed on 20 April 2010].